

Finite element method calculations of ZnO nanowires for nanogenerators

M. A. Schubert,* S. Senz, M. Alexe, D. Hesse, and U. Gösele
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
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The bending of a nonconducting piezoelectric ZnO nanowire is simulated by finite element method calculations. The top part is bent by a lateral force, which could be applied by an atomic force microscope (AFM) tip. The generated electrical potential is ± 0.3 V. This relatively high signal is, however, difficult to measure, due to the low capacitance of the ZnO nanowire ($\sim 4 \cdot 10^{-5}$ pF) as compared to the capacitance of most preamplifiers (~ 5 pF). A further problem arises from the semi-conducting properties of experimentally fabricated ZnO nanowires which causes the disappearance of the voltage signal within picoseconds.

Recently nanogenerators for powering nanodevices were reported in which a ZnO [1], GaN [3] or a CdS [4] nanowire converts mechanical energy into electrical energy on bending the nanowire. In these experiments the nanowires were bent by an AFM tip. Using finite element calculations Gao and Wang [5] calculated a piezoelectric potential in the order of 0.3 V generated by bending a ZnO nanowire. At first sight this high surface potential leaves the impression of an easy measurement and usability. However, in practice there are several limiting factors to be considered. Firstly, the fabricated ZnO nanowires are not perfect insulators, but rather n-doped semiconductors with a typical resistivity of $1 \Omega\text{cm}$. The second problem is related to the actual measurement of the signal generated by the bent nanowire. In the present paper we will address shortly both problems and show that the piezoelectrically generated signals by ZnO nanowires can not easily be detected. We discuss the possibility of measuring the piezoelectric signals and the requirements for energy harvesting.

We calculated the bending of a ZnO nanowire using the program Comsol Multiphysics applying the finite element method (FEM) [6]. The nanowire was modelled as a perfect cylinder (Fig. 1) of 600 nm length and 25 nm radius. The bottom part of the nanowire was fixed and, in order to bend the wire, a lateral force of $F = 80$ nN was applied to the upper part. For electrical boundary conditions we assume a grounded surface element at the bottom and no free charge.

The FEM program solves the following equations:

$$\sigma_p = c_{pq}\epsilon_q - e_{kp}E_k \quad (1)$$

$$D_i = e_{iq}\epsilon_q + \kappa_{ik}E_k \quad (2)$$

where σ is the stress tensor, ϵ the strain, c_{pq} the linear elastic constant, e_{iq} the piezoelectric coefficient, κ_{ik} the dielectric constant, D the electric displacement and E the electric field. We used the elastic and piezoelectric constants for ZnO from literature [5].

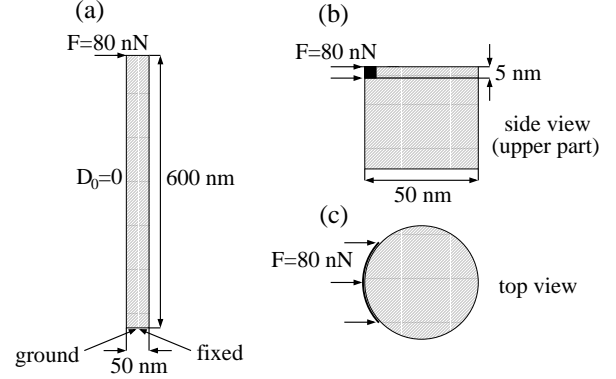


FIG. 1: Schematic model of the ZnO nanowire. (a) Side view of the whole nanowire. Side view (b) and top view (c) of the upper part with the applied force.

An important detail for the FEM calculations is the geometry used to apply the force for bending the nanowire. In literature the nanowire was bent by an AFM tip [1], but in a simulation it is difficult to express this realistically. The simplest method is to use a point force. A force applied in one point is, however, not realistic and has the disadvantage of a non converging solution at this point. In a FEM calculation, the solution is always obtained on only a limited number of points, on the mesh. Thus, the result of the application of a non-physical point force depends on the mesh size. If a tip touches the nanowire, the contact area is at first very small, but in the contact point the maximum loading of the tip is exceeded. Therefore the contact area between the AFM tip and the nanowire increases. To simulate a similar case we use a model of the nanowire which consists of several cylinders stacked on top of each other. The force was applied to a shell element of a small cylinder (height of 5 nm) on top of the nanowire (Fig. 1 (b), (c)).

For an applied force of $F = 80$ nN the maximum bending (lateral deflection of the top) of the nanowire is 133 nm and the electric potential at a height of 300 nm is ± 0.3 V. Figure 2 shows the results of the electric potential for a bent ZnO nanowire, the image on the left side shows the whole wire. On the right side the top part of the nanowire is shown. The electric potential is slightly increased on the left side of the 5 nm high cylinder ele-

*Electronic address: aschub@mpi-halle.mpg.de

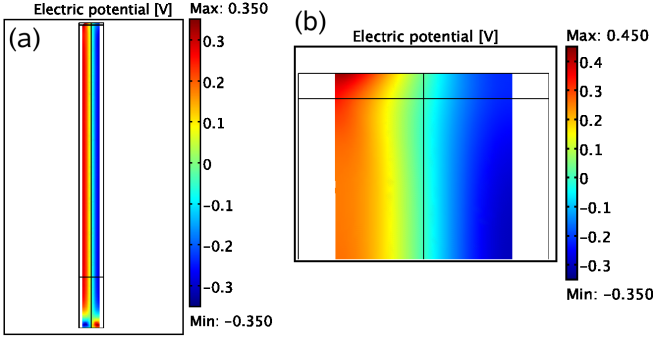


FIG. 2: FEM calculation of a ZnO nanowire bent by a lateral force of 80 nN. (a) the whole nanowire; (b) upper part of the nanowire. Here, the electric potential on the shell element with the applied force is slightly higher than in the rest of the nanowire. Note that the scale is different in both images and that the nanowire is shown with its undistorted shape.

ment on top of the nanowire, at the place of the applied force.

As the constitutive equations of the piezoelectric effect show [7], a piezoelectric sensor works in converse piezoelectric mode and generates only charge for a certain applied strain. Therefore, a piezoelectric nanowire can not be regarded as a voltage source, but rather as charge generator. In order to estimate the charge that will generate the calculated potential we need to estimate the capacitance C of the nanowire. Using the parallel plate capacitor approximation of a nanowire with lateral electrodes as in Fig. 3, C is given by:

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (3)$$

where $\epsilon_0 = 8.854 \cdot 10^{-12} \text{ F} \cdot \text{m}^{-1}$ is the vacuum permittivity and $\epsilon_r = 8.91$ the permittivity of the ZnO nanowire. For the area A of the capacitor we use a height of 500 nm and a width of 50 nm and for the distance d the same value as for the width. For the above dimension the capacitance of the nanowire (nw) is

$$C_{nw} = 3.9 \cdot 10^{-17} \text{ F}$$

and the charge Q on the nanowire that will generate the calculated potential should be

$$Q_{nw} = C_{nw} \cdot U_{nw} = 1.2 \cdot 10^{-17} \text{ C}.$$

The above values are calculated assuming the most advantageous case when the electrodes are deposited on the sidewalls of the nanowire, and the whole generated charge is collected for the signal generation. In real experiments an AFM tip was used to bend the nanowire and also to collect the signal [1]. In this case the capacitor area is equal to the tip sample contact area and it is several orders of magnitude smaller than above. Therefore, to compare to real experiments we should assume a contact area of around 200 nm^2 . Thus, the effective capacitance will be reduced by a factor of 100 to

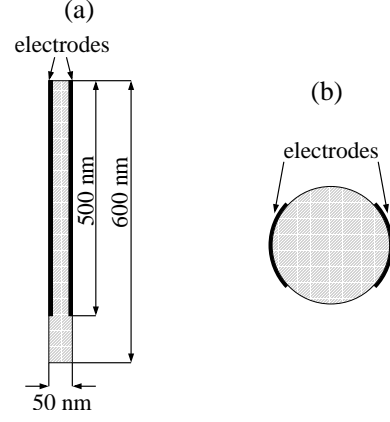


FIG. 3: ZnO nanowire with electrodes on the sidewalls. (a) Side view and (b) top view of the nanowire.

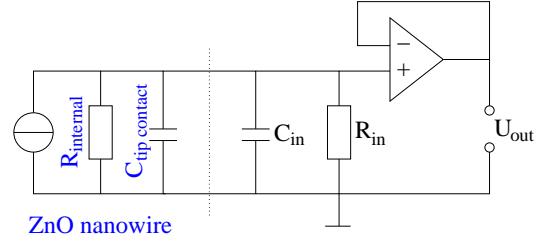


FIG. 4: Circuit with an amplifier for measuring the signal generated by a bent ZnO nanowire. $R_{internal} = \infty$ in the ideal case of a nonconducting nanowire. ($R_{in} = 100 \text{ M}\Omega$, $C_{in} = 5 \text{ pF}$)

about $C_{tip \text{ contact}} \approx 4 \cdot 10^{-19} \text{ F}$, likewise the charge, that will be collected by the AFM tip, which is now $Q_{tip \text{ contact}} \approx 1.2 \cdot 10^{-19} \text{ C}$ ($U_{tip \text{ contact}} \approx U_{nw}$). The above rough estimation gives a signal equivalent to one electron that should be collected by the AFM tip. Using the FEM calculation we estimated the charge of a cylindric nanowire with electrodes on the sidewalls as given in Fig. 3 and for the AFM tip contact with the same area as for the applied force. The results calculated using FEM confirm our rough estimation ($Q_{nw \text{ FEM}} = 1.7 \cdot 10^{-17} \text{ C}$ and $Q_{tip \text{ contact FEM}} \approx 1.7 \cdot 10^{-19} \text{ C}$).

Even in the case of an ideal nonconducting ZnO nanowire, it is very difficult to transform the 0.3 V electric potential in an output signal. This potential is generated only by connecting an external circuit to this point (top of the nanowire). A typical external circuit using an amplifier is given in Fig. 4. Most preamplifiers have an input capacitance of $C_{in} \sim 5 \text{ pF}$, but the capacitance of the nanowire using an AFM tip as electrode is only about $4 \cdot 10^{-17} \text{ pF}$. Considering the most advantageous situation of a direct coupling between the nanowire and the amplifier input, from the charge conservation one can calculate the voltage at the preamplifier input:

$$Q = C_{tip \text{ contact}} \cdot U_{tip \text{ contact}} = C_{in} \cdot U_{in}. \quad (4)$$

This shows that in reality the calculated potential of

0.3 V generates a signal of only 20 nV. To measure such a low voltage represents quite a challenge. The signal increases to 2 μ V when the sidewalls of the ZnO nanowire are used as electrodes (as plotted in Fig. 3).

Until now we discussed only an ideal non-conducting ZnO nanowire. However, in reality the fabricated ZnO nanowires are n-doped semiconductors with a typical resistivity of 1 Ω cm. This value can be estimated from the I-V characteristics given in literature [1, 8]. The recent literature on ZnO nanowires confirms that the typical resistivity values are in a range of 10^{-2} Ω cm to 10 Ω cm. The distribution of the potential as shown in Fig. 2 suggests that the piezoelectrically generated charge is distributed on the sidewalls and the resulting electric field points perpendicular to the nanowire axis. Therefore, the effective resistance should be calculated accordingly:

$$R = \rho \cdot \frac{l}{A} \quad (5)$$

where l is the nanowire diameter and A the cross section of the wire, in the approximation of a square wire. This will give an effective resistance of 20 k Ω for $\rho = 1$ Ω cm.

FEM calculation gives a similar value of the resistance ($R = 22.5$ k Ω). As we mentioned, the piezoelectric effect generates charge and the time dependence of the generated voltage can be calculated, using the classical textbook equation for an RC circuit.

$$u(t) = U_0 \cdot e^{-\frac{t}{RC}} \quad (6)$$

where $u(t)$ is the time-dependent output voltage, U_0 the initial voltage, t the time and $\tau = R \cdot C$ is the discharging time constant. After the time τ the output voltage decreases to 1/e of its initial value. For the ZnO nanowire we obtain a discharging time constant of $\tau = 7.8 \cdot 10^{-13}$ s using the estimated value of the charge and the resistivity. For the values calculated using the FEM we obtain: $\tau_{FEM} = 1.3 \cdot 10^{-12}$ s. This means simply that in only a few picoseconds the charge generated by the piezoelectric effect will be cancelled by internal losses.

In the experiments reported in the literature, the nanowires were bent by an AFM tip with a limited scan speed. For a scan speed of 100 μ m/s the ideal nanowire is completely charged after a time $t_0 = 1.3$ ms. The charge

on the nanowire increases nearly linearly during bending the wire. Therefore we can calculate the charge current $I_c = dq/dt$ for an ideal nanowire with electrodes on the sidewalls ($Q_{nw} = 1.2 \cdot 10^{-17}$ C) during bending:

$$I_c = \frac{Q_{nw}}{t_0} = 9.0 \cdot 10^{-15} \text{ A.}$$

In the case of a real ZnO nanowire most of the charge current flows through the resistor and does not charge the electrodes. For a conductive nanowire ($R_{nw} = 20$ k Ω), the electric potential is thus reduced from 0.3 V to:

$$U_{real} = R_{nw} \cdot I_c = 1.8 \cdot 10^{-10} \text{ V.}$$

In summary, using FEM calculations we have analyzed a bent ZnO nanowire and we obtained a piezoelectrically generated electric potential of about 0.3 V. This seems to be an easily readable signal, but in practice there are important obstacles, even for an ideal ZnO nanowire. The first is the very low capacitance of the nanowire in case of the AFM tip contact ($4 \cdot 10^{-7}$ pF) compared to the input capacitance of a typical preamplifier (5 pF). The corresponding charge generated by the nanowire is in the order of the elementary charge. According to charge conservation the input voltage at the preamplifier is reduced from 0.3 V to about 20 nV. In an ideal case with electrodes on the sidewalls of the nanowire the input voltage at the preamplifier is about 2 μ V. Further problems arise for a real ZnO nanowires, because these wires are not perfect insulators, but rather n-doped semiconductors with a typical resistivity of less than 1 Ω cm. Due to this high conductivity the charged nanowire is discharged within picoseconds. During bending the nanowire with an AFM tip (at a scan speed of 100 μ m/s) the electric potential on the nanowire is thus reduced from 0.3 V to $U_{real} = 1.8 \cdot 10^{-10}$ V as a result of a nonrelativistic calculation. This means that a real ZnO wire has probably no charge, during and after bending with an AFM tip. This makes it nearly impossible to measure a piezoelectric signal of a real ZnO nanowire, in spite of reports to the contrary in the literature [1, 2, 4, 9].

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